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CHEMICAL REACTIVITY OF HYDROGEN, NITROGEN AND OXYGEN
ATOMS AT TEMPERATURES BELOW 100° K

by

H. A. McGee, Jr. (Principal Investigator)
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J. H. Wilson

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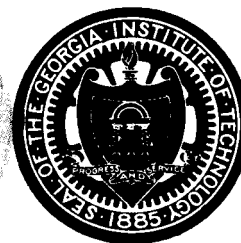
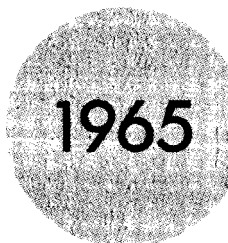
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ABSTRACT

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The question of the possible free existence of low molecular weight compounds of divalent carbon is interesting from the point of view of the chemistry of both the comets as well as the atmospheres and surfaces of the Jovian planets. CF_2 , although not itself of direct interest, is nevertheless the species of divalent carbon that is most likely to be stabilized by cryogenic techniques. We have produced CF_2 by the pyrolysis of CF_3I on hot metal filaments, and its ionization energy has been determined to be 11.8 ± 0.1 ev. Many other appearance potentials (AP) and ionization potentials (IP) of fragments from CF_3I and several other possible parent substances for the production of CF_2 have also been measured, usually to within ± 0.1 ev. A search was made for the free existence of CF_2 and CF_3 at temperatures down to 4.2°K . The cryogenic inlet system to the mass spectrometer that has been described earlier was used for this purpose. In one experiment, CF_3^+ (mass 69) was observed as the heaviest mass in the vapor over the quenched pyrolysis products at a temperature only slightly above that of liquid nitrogen. The obvious and exciting hypothesis that the CF_3 was being resublimed in a chemically unchanged state was disappointingly short lived when it was found that the AP of CF_3^+ in this experiment was very nearly the AP of CF_3^+ from CF_4 . CF_4 does not exhibit a parent peak. Concurrent work in other laboratories has supported the conclusion that CF_2 is not chemically stable at cryogenic temperatures. Hence, the existence of CH_2 in chemically significant concentrations in comets, etc., is unlikely, and leaves matrix isolation as a probable means of the occurrence of very minute amounts of the species.

Author

Atomic hydrogen has been reacted with very pure NO in cryogenic reactors. With solid NO at 77° K, a yellow solid is produced which seems to explode on warming. With NO in solution in liquid propane at 90° K, a similarly appearing yellow precipitate is formed which also seems to explode on warming. Oxygen atoms react with solid NH₃ at 90° K to form a light yellow substance. At 77° K, this same reaction initially produces a light yellow layer, but as O₃ from the discharged O₂ is condensed into the NH₃, the yellow color becomes more intense and finally changes to an orange color. Tentative reaction mechanisms are proposed and further work is outlined which will elucidate more fully these very low temperature reactions.

I. INTRODUCTION

There are several problems within the broad area of chemical reactivity at cryogenic temperatures that are to be examined during the course of this investigation. In the order of their performance in a typical experiment, these include (1) generation of suitable reactants or precursors, (2) low temperature reactions, (3) purification of products, and (4) identification and characterization, by their elementary physical and chemical behavior, of selected product substances. A few sentences on each of these problems will serve to introduce the technical discussion in succeeding chapters of this report.

(1) Very few substances will react upon contact at cryogenic temperatures,¹ but rather most require some manner of activation. An interesting instance of direct reactivity is the H_2 - F_2 system, wherein instantaneous ignition occurs when H_2 gas is bubbled beneath the surface of liquid F_2 and, more interestingly, solid F_2 and liquid H_2 will explode on contact at 20° K. In the present studies we are concentrating on two schemes of activation for the generation of suitable precursors, electrodeless glow discharge and pyrolysis.

(2) The reactor designs have been such as to quench or trap some species from the above activation process, or to react the effluent from the activation process with a second substance which is already in the cold reactor, or to contact the active species with the second reactant in the vapor phase followed by a rapid quench (i.e., a sort of quenched diffusion flame arrangement).

¹McGee, H. A. Jr., and Martin, W. J., Cryogenics **2**, 257 (1962).

(3) Purification techniques using continuous fractional sublimation and recondensation which we call "thermal chromatography" are being developed. Presumably adsorption and absorption schemes also are possibilities. Absolute temperature control both in the reactor and in the subsequent processing is essential since the products are often unstable at some still very low temperature.

(4) Identification of product substances is accomplished mass spectrometrically utilizing a cryogenically cooled sample inlet system. The mass spectrometer is also used to follow the chemistry occurring during warm-up as well as to measure the appearance potentials and ionization potentials of species of interest, usually to within an accuracy of ± 0.1 ev.

The motivation for the choice of systems to study is based on considerations from space chemistry. For example, it is now generally realized that any real understanding of chemical processes occurring on certain objects of astronomical interest, must be realized in terms of cryochemistry. As immediate examples of this, one may recall the "dirty snowball" model of comets and the atmospheric chemistry of the Jovian planets.

A rather broad literature review including many experiments in cryochemistry and containing over 200 references has been prepared by McGee and Martin.¹ It is our objective to restudy and to expand upon some of these earlier observations of cryogenic chemical reactivity.

II. CURRENT STATUS OF RESEARCH

A. Ionization and Appearance Potential Measurements

The experimental determination of ionization potentials is important for the numbers are useful in thermochemistry, in kinetics, and other areas

of chemistry and chemical physics. More specifically, for the case of the unusual chemical behavior at very low temperatures that is of concern here, the data may be applied to identification problems, to molecular structure problems and to unusual chemical kinetic problems.

Our procedure for the experimental determination of the appearance and ionization potentials employs the Fox retarding potential difference (RPD) method and has been described in detail in earlier reports.² This method is well suited for use with the Bendix T-O-F mass spectrometer and is generally thought to be the most accurate method available for the measurement of appearance potentials by electron impact techniques without going to very elaborate apparatus to produce monochromatic beams.

The species CH is first seen in comet head spectra at 1.5 A.U., so the existence of low molecular weight but reactive molecules containing carbon which might be stable at some very low temperature would be a significant factor in arguments about the chemistry of comets. Many theories have been proposed for the nature of the comet nucleus, but the most generally accepted one is Whipple's "dirty snowball" model, i.e., the nucleus is assumed to be composed of meteoric dust and ices of H_2O , CH_4 , NH_3 , H_2O_2 , etc. The icy nucleus on passing near the sun, will sublime and release the frozen species in ratios and in rates dependent upon their relative volatility. Occasionally ruptures or even chemical explosions will occur in the nucleus which will produce the jetting action and the halo formations that have been observed. The most puzzling molecules which have been spectroscopically detected are CN and C_3 since it is not

²McGee, H. A. Jr., Second Semiannual Technical Report, Grant NsG-337, March 1, 1964.

clear how these species could be formed from CH_4 , NH_3 , H_2O_2 , etc. This then is the origin of our interest in carbon containing species.

The species CF_2 , although not of cometary significance, might exist as a stable entity at low temperatures. At ordinary temperatures it is by far the most stable compound of divalent carbon, and it hence seemed a reasonable starting place which would lead to similar studies of molecules of more direct relevance.*

There has recently been considerable interest in the formation and stability of CF_2 and of various other methylenes and substituted methylenes.³ These species appear to be present as intermediates in a number of reactions and, in particular, several studies have indicated that CF_2 is produced in the photolysis, pyrolysis or electrical discharge of fluoro-carbon vapors. The emission⁴ and absorption^{5,6,7,8} spectra of CF_2 have been reported and partially analyzed⁴ and, lately, the vibrational assignments have been revised to some extent.^{6,7,8} Mass spectrometric identification of CF_2 has

*The CF_2 and Cl_2 work constituted the Ph.D. thesis of Mr. W. J. Martin. Copies of this thesis will be forwarded to NASA by March 1, 1965. The following few pages of this report summarized some of the highlights of this study.

³A review of this work is contained in: J. Hine, "Divalent Carbon," Ronald Press, New York, 1964.

⁴P. Venkateswarlu, Phys. Rev. **77**, 676 (1950).

⁵R. K. Laird, E. B. Andrews and R. F. Barrow, Trans. Faraday Society **46**, 803 (1950).

⁶D. E. Mann and B. A. Thrush, J. Chem. Phys. **33**, 1732 (1960).

⁷A. M. Bass and D. E. Mann, J. Chem. Phys. **36**, 3501 (1962).

⁸D. E. Milligan, D. E. Mann, Marilyn E. Jacox and R. A. Mitsch, J. Chem. Phys. **41**, 1199 (1964).

also been reported,⁹ but the value, 13.3 ev, which was claimed for the ionization potential of CF_2 , $I_{\text{vert}}(\text{CF}_2)$, is significantly different from that determined in this study. The half-life of CF_2 , as formed in one of the above experiments, was estimated to be of the order of one second.⁵ CF_2 , generated in an electric discharge, has been trapped in an argon matrix at liquid helium temperatures,⁷ and the species has been similarly trapped when generated by the photolysis of difluorodiazirine, CF_2N_2 , in a matrix of argon or nitrogen.⁸ An extraordinary chemical stability of CF_2 has been invoked by Mastrangelo¹⁰ to explain experiments in which the products of a radio frequency discharge through C_2F_6 or cyclo- C_4F_8 were deposited on a liquid nitrogen cooled surface. A blue color, claimed to be due to CF_2 , persisted up to 95° K. However, CF_2 in solid argon at 4.2° K, will disappear with the formation of C_2F_4 when the solid is annealed at only 40° K. This could be due to a greater mobility of CF_2 in the A matrix, but in any event, the chemical stability of CF_2 relative to C_2F_4 is apparently not large.

In the course of our investigation of the stability of methylene and its low molecular weight derivatives at temperatures below 100° K, CF_2 has been generated from a new source and its I_{vert} has been measured. Thermochemical numbers of this sort enter into arguments that are developed from the point of view of the energetics that are involved in studying the low temperature chemical behavior of these species.

⁹R. I. Reed and W. Snedden, Trans. Faraday Soc. **54**, 301 (1958).

¹⁰S. V. R. Mastrangelo, J. Am. Chem. Soc. **84**, 1122 (1962).

The apparatus used for the production and identification of CF_2 is shown schematically in Fig. 1. A gas mixture containing CF_3I and A was fed onto a heated filament and passed directly into the ionization region of the mass spectrometer. The filament was positioned approximately 1/4 inch from the ionizing electron beam. At the pressures (10^{-4} - 10^{-5} torr) at which the hot filament region was operated, the mean free path of the newly formed CF_2 was estimated to be of the order of 10 cm. Hence, an essentially collision-free path should exist between the filament and the mass spectrometer ionization region.

A Bendix Model 12-101 Time-of-Flight Mass Spectrometer was used in this work with minor modifications to permit the determination of appearance potentials (AP). AP lowering is considered to be the most reliable mass spectrometric method for the detection of unstable species in a gaseous mixture.¹¹ The retarding potential difference (RPD) method due to Fox, et al.¹² was employed for these measurements, and Melton and Hamill¹³ have given complete instructions for the use of the RPD technique with the Bendix machine. The various potentials were measured by a Cimron Model 6000 digital voltmeter, that was periodically checked against a good Leeds and Northrup potentiometer.

The filament current was controlled by a Powerstat and a constant voltage transformer. Fine control was obtained by use of a slide wire resistor in series with the filament. The filament temperature was measured with a Leeds and Northrup model 8622-C optical pyrometer.

¹¹F. P. Lossing, "Mass Spectrometry," (C.A. McDowell, ed.), McGraw-Hill Book Company, New York, 1963, p. 442.

¹²R. E. Fox, W. M. Hickam, D. J. Grove and T. Kjeldaas, Jr., Rev. Sci. Instr. **26**, 1101 (1955).

¹³C. E. Melton and W. H. Hamill, J. Chem. Phys. **41**, 546 (1964).

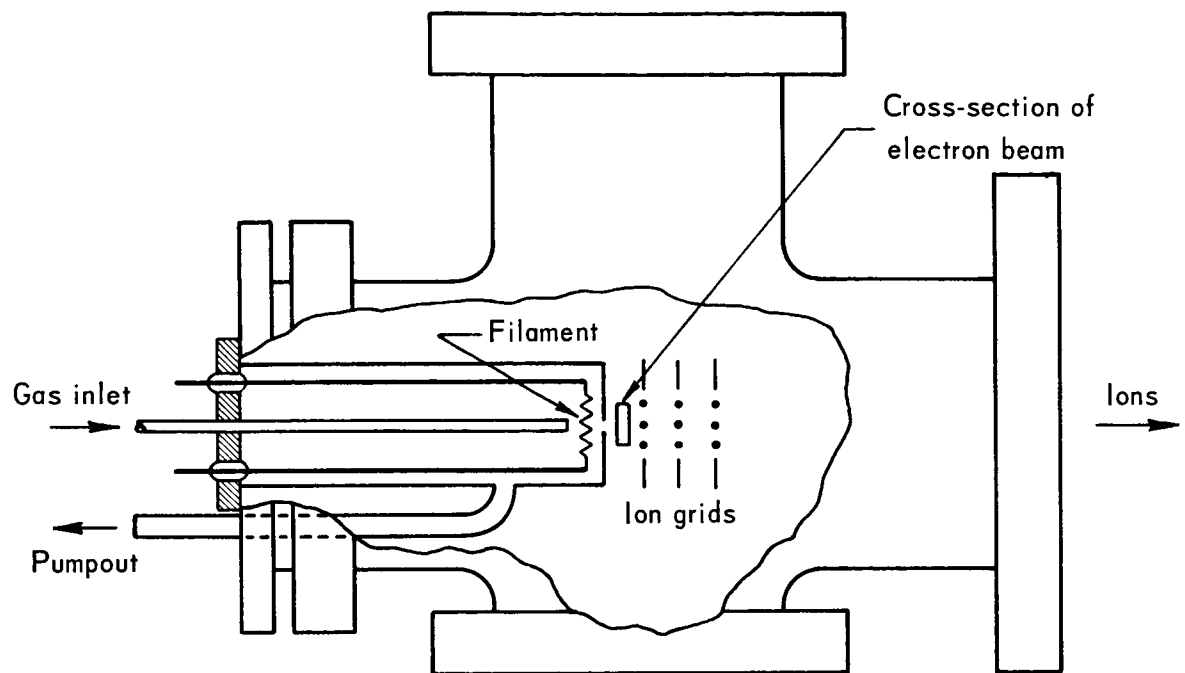


Figure 1. Schematic of hot filament inlet and ion source arrangement.

When CF_3I was admitted to the mass spectrometer with the hot filament inlet system at room temperature, $\text{AP}(\text{CF}_2^+)$ was found to be 17.2 ± 0.1 ev. With a platinum filament at a temperature of $900^\circ\text{--}1300^\circ\text{C}$ the CF_2^+ peak was observed at much lower electron energies. CF_2 was present in such quantity that the vertical IP could easily be determined and was found to be $I_{\text{vert}}(\text{CF}_2) = 11.8 \pm 0.1$ ev. This value is in good agreement with that recently obtained by Fisher, Homer, and Lossing.¹⁴ The thermochemical quantities that were developed by FHL and which depend upon $I_{\text{vert}}(\text{CF}_2)$ are all supported by this work. The ionization efficiency curve for CF_2^+ is shown in Fig. 2, along with the corresponding curve for the calibrating gas, argon. The break in the curve at 12.8 ev. apparently corresponds to the production of CF_2^+ in an excited electronic state. This ionization efficiency curve is typical of the appearance of those that have been developed in this laboratory for many species produced from the fragmentation and pyrolysis of a series of halo-carbons. Many candidates for suitable parent substances for the production of CF_2 were investigated before CF_3I was found.

The uncertainty attached to the ionization energy applies to I_{vert} , since the actual ionization energy is not necessarily observed in electron impact experiments.

The use of a tungsten, rather than a platinum, filament yielded no evidence for the presence of CF_2 , which indicates that the production process involves the nature of the filament in some manner; i.e., surface chemistry effects are occurring. It also appeared that the CF_2 producing

¹⁴I. P. Fisher, J. B. Homer and F. P. Lossing, private communication and J. Am. Chem. Soc., in press.

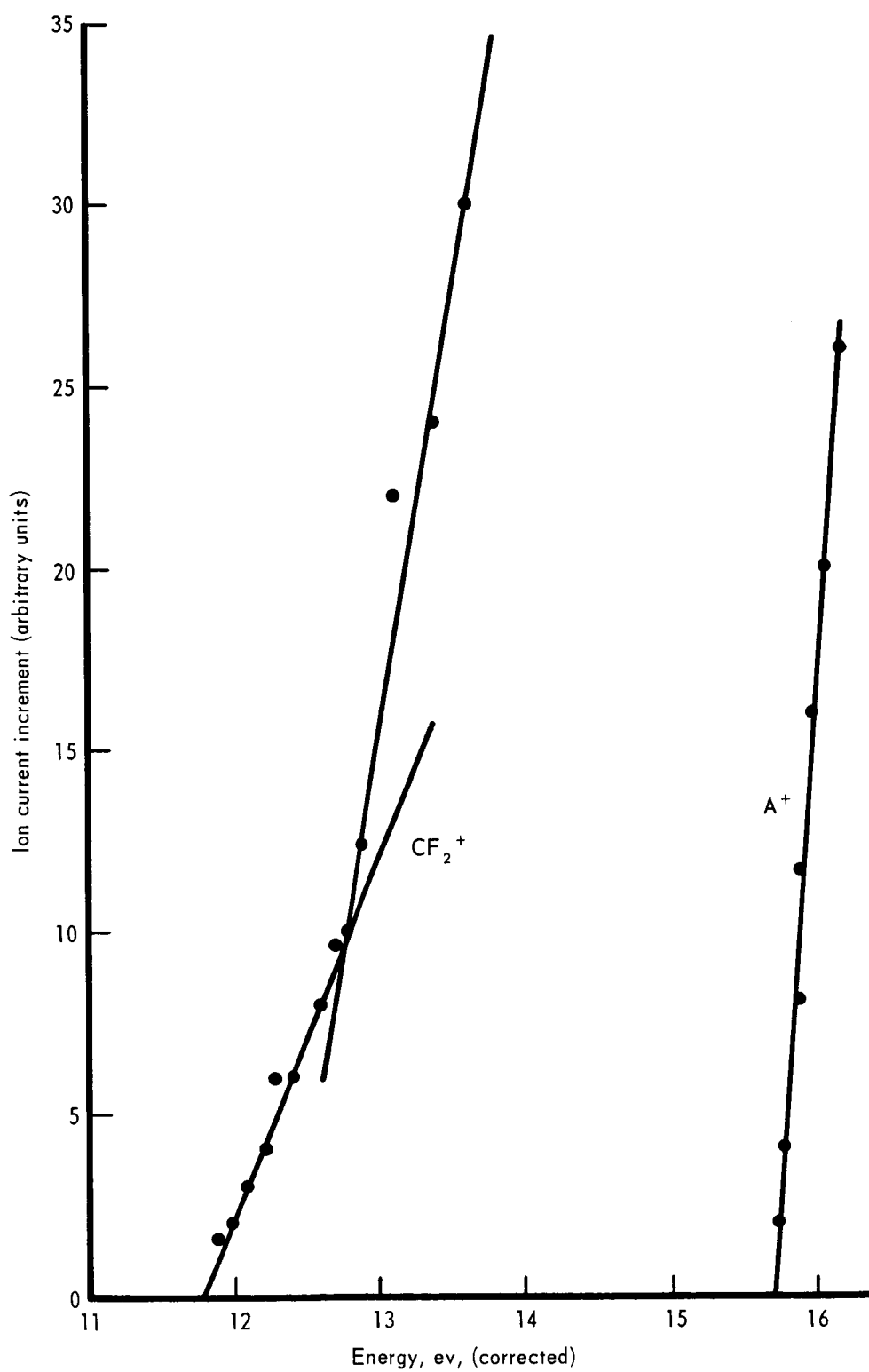


Figure 2. Ionization efficiency curve for $I_{\text{vert}}(CF_2)$. The ion current is actually the difference ion current obtained from the retarding potential difference.

capacity of a platinum filament was destroyed by long use or by use with other fluorocarbon gases. $AP(CF_3^+)$ from the CF_3I was found to be 11.1 ± 0.1 ev. The vertical ionization potential of CF_3 has been reported to be as high as 10.2 ev,¹⁵ and hence it is clear that the detection of CF_3 by AP lowering will be difficult since the AP and the IP are so close together. However, the presence of considerable concentrations of C_2F_6 and I_2 that were observed in these pyrolysis gases would seem to indicate that CF_3 was formed during this process. Previous studies of the pyrolysis and photolysis of CF_3I have shown that CF_3 radicals are produced, but the absorption spectrum of CF_2 could not be detected in the photolysis of CF_3I .¹⁶ The incandescent platinum filament lowered $AP(I^+)$ from about 13 ev to 8.8 ± 0.1 ev. This lower value corresponds to $AP(I^+)$ from I_2 .¹⁷

B. Low Temperature Quenching Experiments with CF_2

Quenching experiments on the CF_2 produced in the pyrolysis of CF_3I were conducted in the cryogenic inlet system described in an earlier report, and they utilized both liquid nitrogen and liquid helium as refrigerants. Since most of the experiments were conducted at liquid nitrogen temperature, this phase of the work is discussed first.

¹⁵F. P. Lossing, P. Kebarle and J. B. de Sousa: "Advances in Mass Spectrometry," (J. Waldron, ed.), Pergamon Press, New York, 1959, p. 431.

¹⁶G. Porter, Discussions Faraday Soc. 14, 133 (1953).

¹⁷D. C. Frost and C. A. McDowell, "Advances in Mass Spectrometry," (J. Waldron, ed.), Pergamon Press, New York, 1959, p. 413.

In order to duplicate as closely as possible the conditions of the experiments which resulted in the production of CF_2 (as described above) the parent compound was decomposed on a platinum filament which was set to approximately 1100°C and argon was used as a carrier gas. The filament was located inside the high temperature pot (HTP) of the cryogenic inlet system (CIS) and within one-half inch of the cold walls of this chamber.* During the pyrolysis, HTP, the gradient tube and LTP were maintained at liquid nitrogen temperature so that the condensation of the hot gases was affected very close to the filament. The cracking and subsequent quenching were conducted for periods of from one-half to one hour. That this yielded an almost complete condensation of all the pyrolysis products was evidenced by the fact that in only one run was a faint spectrum due to one of these products observed while the low temperature pot (LTP) was still at liquid nitrogen temperature.

After the flow of parent gas was stopped and the hot filament turned off, the temperature of HTP was allowed to increase (usually only about 50°) while that of LTP was held at liquid nitrogen temperature. This resulted in a temperature drop along the gradient tube and, hence, in some degree of separation of the pyrolysis products, as the more volatile species migrated down the tube toward lower temperatures. The entire inlet system was then allowed to warm slowly, while maintaining the temperature gradient, and the effluent gases were monitored (with no further warming) by the mass spectrometer. The spectra of the gases were

* By way of review of earlier reports, one should recall that the CIS consists basically of two independently thermostated pots (HTP and LTP) connected by a tube upon which there is impressed the gradient $T_{\text{HTP}} - T_{\text{LTP}}$. A capillary leak on LTP admits the cold sample directly into the ionizing electron beam of the T-O-F mass spectrometer in a manner not allowing warm-up of the sample prior to ionization.

recorded at various temperatures and the use of a discriminating low energy electron beam was employed to search for free CF_2 and CF_3 .

Table I lists the fluorocarbon gases whose mass spectra were identified during the warmup and the temperature of the inlet system at the time at which these spectra were recorded. The major products were found to be CF_4 , C_2F_4 , C_2F_6 , I_2 and the unchanged parent, CF_3I .

TABLE I
GASES IDENTIFIED DURING WARMUP (LIQUID NITROGEN QUENCH)

Gas	Temperature Interval During Which Spectrum First Appeared		
	Run 1 [*]	Run 2	Run 3
CF_4	-196° C	-196° C to -188° C	-190° C to -187° C
C_2F_4	not detected ^{**}	-188° C to -162° C	-170° C to -160° C
C_2F_6	-196° C to -150° C	-188° C to -162° C	-170° C to -160° C
CF_3I	-150° C to -142° C	-157° C to -148° C	-149° C to -142° C

* Did not record spectra between -196° C and -150° C.

** C_2F_4 was present in gases coming through the inlet system while it was being cooled simultaneously with conduct of pyrolysis. The condensed C_2F_4 must have vaporized and have been pumped out of the system in the interval between -196° C and -150° C.

CF_4 had not been previously identified in the pyrolysis studies because of the absence of a parent peak in its mass spectrum. The predominant peak in the CF_4 spectrum is that due to CF_3^+ (mass 69) and the observation of this mass, at a temperature only slightly above that of liquid nitrogen,

led to the initial hypothesis that the CF_3 free radical was being trapped and revaporized without reaction or recombination. However, this exciting result was short lived since rough appearance potential studies of this low temperature gas demonstrated that this spectrum resulted from electron impact fragmentation of the CF_4 molecule. The approximate appearance potentials of CF_2^+ and CF_3^+ from this work and the corresponding values from Reed and Snedden's study of CF_4 ⁹ are given in Table II, where $I_{\text{vert}}(\text{CF}_2)$ and $I_{\text{vert}}(\text{CF}_3)$ are also given. Obviously, the first gas which is evolved during warmup must be characterized as CF_4 rather than CF_3 .

TABLE II
AP OF CF_2 AND CF_3 FROM THE LOW TEMPERATURE VAPOR

	AP Obtained in this Work (uncorrected)	AP from CF_4 (ref.9)	I_{vert}
CF_2	23 ± 2 ev.	22.33 ± 0.06 ev.	11.8 ev.
CF_3	16 ± 2 ev.	15.4 ± 0.05 ev.	10.2 ev.

At somewhat higher temperatures (about -160°C), C_2F_4 and C_2F_6 began to appear in the effluent gases from the cryogenic inlet system. The relative proportions of these gases varied from one run to another but each was present in every case. After the inlet system had warmed to about -150°C the spectrum of the unchanged CF_3I appeared; at approximately -140°C the parent compound had become the major contributor to the mass spectral pattern.

At various temperatures throughout these warmup experiments the ion currents due to the CF_2^+ and CF_3^+ ions were observed at electron energies intermediate between their ionization potentials and their appearance potentials from CF_4 . In no case was there found any evidence for the presence of free CF_2 or CF_3 . $\text{AP}(\text{CF}_3^+)$ did, in fact, drop to approximately 11 eV but this change was found to occur at very nearly the same temperature as that at which CF_3I began to appear in the spectrum of the warmup products ($\text{AP}(\text{CF}_3^+)$ from $\text{CF}_3\text{I} = 11.1$ eV).

In an additional series of experiments, liquid helium was used as a refrigerant in the cryogenic inlet system. The same pyrolysis techniques were employed but in these experiments the argon: CF_3I ratio was considerably larger (about 10:1.). At 4.2° K the argon serves not only as a carrier gas but also as an inert matrix for the trapping of the unstable species.

In these experiments, deposition of the pyrolysis products was limited to 10-15 minutes since it was found that the cost of maintaining the system at 4.2° K was prohibitive. The cryogenic inlet system had been designed for use at liquid nitrogen temperature and a complete reconstruction would be required in order to run the system for the periods of time (about one hour) which were used for deposition in the experiments conducted at 77° K. The much smaller deposits (due both to dilution and to shorter runs) proved to be a handicap in the analysis of the warmup products since much less gas was evolved and pumped through the mass spectrometer.

The mass spectra which were recorded during the warmup of these deposits again showed the presence of C_2F_4 , C_2F_6 and CF_4 but these experiments yielded no evidence for the presence of free CF_2 or CF_3 in the low

temperature gas above the condensed phases which had been deposited at 4.2° K.

As mentioned earlier, two recent publications ^{7,8} have discussed the spectroscopic study of CF_2 trapped in an argon matrix at liquid helium temperature. One of these studies, ⁸ which was published in September, 1964, showed that on warming to 40° K, the argon matrix softened sufficiently to permit diffusion and consequent dimerization of the trapped CF_2 . After the warmed products were again cooled to 4.2° K, the spectrum of CF_2 was completely gone but that of C_2F_4 was much more intense. A personal communication from one of the authors of this latter study included this further amplification: "These studies have shown, for example, that even though CF_2 is readily formed from disfluorodiazirine at 4° K in both argon and nitrogen matrices (Inert: $\text{CF}_2\text{N}_2 = 200:1$) and can be maintained in the matrix without C_2F_4 formation for hours, at a temperature of 14° K, C_2F_4 formation is complete."* The fact that this reaction goes to completion at, or below, 14° K indicates that the activation energy for the combination of two CF_2 molecules is extremely small and, hence, that it is highly unlikely that relatively pure samples of condensed phase CF_2 can be prepared, even at the lowest obtainable temperatures. In any event, in the present experiments, if we assume that the CF_2 survived the quench, it must have been chemically lost at temperatures well below that at which the species had enough energy to exert a vapor pressure of 10^{-5} to 10^{-6} mm Hg.

* The authors are indebted to Dr. R. A. Mitsch of Minnesota Mining and Manufacturing Company, Saint Paul, Minnesota for this comment.

Mastrangelo¹⁰ has studied the deposits formed by quenching to liquid nitrogen temperature the products of a radio frequency discharge in C_2F_6 or cyclo- C_4F_8 . From chemical evidence, it was claimed that CF_2 was present in a red deposit whose color persisted to approximately 107° K. These assignments were based on an analysis of the warmed products which resulted from chlorination and bromination of the low temperature deposits; no direct observation of CF_2 or CF_3 either at the low temperature or after warmup was reported. To reconcile these hypotheses with the more recent spectroscopic data and with the present mass spectral data, one must assume that the matrices formed by the parent compounds used in this study do not soften and permit diffusion of the reactive species until a considerably higher temperature than is the case in an argon matrix.

The present work, in which the pyrolysis products of CF_3I were immediately quenched to 77° K or to 4.2° K, has yielded no evidence for the presence of free CF_2 or CF_3 in the warm up gases. Since Milligan, et al. have shown that CF_2 is indeed trapped in an argon matrix at liquid helium temperature and Mastrangelo¹⁰ has presented arguments for the stabilization of both CF_2 and CF_3 in a matrix of the parent, cyclo- C_4F_8 , at liquid nitrogen temperature, it is very likely that CF_2 and CF_3 are present in the low temperature deposits produced in this work. One again concludes, therefore, that these species must achieve sufficient mobility in the matrices to permit reaction or recombination at temperatures which do not allow sublimation of the free species.

One must also conclude that the existence of CH_2 in significant concentrations (greater than a few tenths of one per cent) in comet nuclei is

very unlikely since CH_2 is less stable relative to C_2H_4 than is CF_2 relative to C_2F_4 .

C. Reactions of Atomic Hydrogen

In this series of experiments atomic hydrogen is produced in an electrodeless discharge arrangement and pumped into a cold reactor. Here the atomic hydrogen is made to (1) impinge upon the free liquid or solid surface of the second reactant or (2) to mix with the second reactant in the gas phase just prior to condensation.

1. Impedance Matching Network

For maximum power transfer and hence maximum production of atomic hydrogen the rf transmitter must be matched to the plasma. The impedance of the plasma is a function of the nature of the gas being excited, the pressure (i.e., the particle number density) and the flow rate. It was hence necessary to design an impedance matching network having a rather wide range of operability. The circuit is shown in Fig. 3 where those components enclosed in dashed lines are mounted in a 17 x 13 x 4 in. box which is itself mounted within 6 in. of the discharge tube on the vacuum rack. The 50 ohm coaxial lead from the transmitter is about 10 ft. long.

The output impedance of the transmitter is 50 ohms and therefore it is necessary to adjust the two capacitors until the impedance of the coil system with its plasma core appears as 50 ohm. The impedance match (or mismatch) is indicated by the standing wave ratio (SWR) meter. The standing wave ratio is defined,

$$(P_F + P_R)/(P_F - P_R)$$

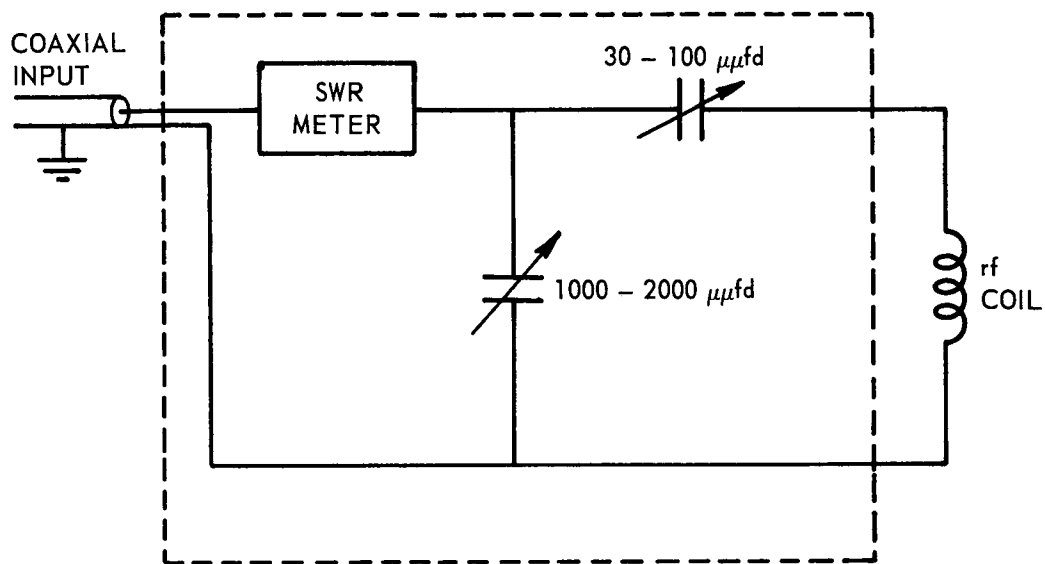


Figure 3. Impedance Matching network.

where P_F is forward power and R_R is reflected power. At an SWR of unity, there would be no reflected power and the impedances would then be perfectly matched. The atomic hydrogen is presently being produced at a forward power level of about 300 watts and a SWR of about 1.1. This corresponds to a reflected power of 15 watts or corresponds to a power use efficiency of 95%.

Using the described matching network, an intense red hydrogen discharge can be maintained up to a pressure of about 80 mm Hg. The inability to produce the intense discharge at higher pressures is probably due to power limitations of the transmitter.

Since the present matching network provides the means for obtaining maximum power transfer at any pressure, the design and construction of the discharge system is now considered complete.

2. Experimental Results

The position and arrangement of the rf discharge coil has again been changed. The coil is wound on an outer pyrex tube of 33 mm outside diameter. The discharge is produced in a concentric 12 mm diameter quartz tube and compressed air is blown into the annular space to provide cooling. This concentric tube arrangement is necessary for the prevention of high voltage arc-over from the coil to the plasma resulting in a puncture of the pyrex or quartz tube. The coil presently in use is made of fifty turns of 14 gauge copper wire. With the series capacitor set at 40 μf and the parallel capacitor set at 2000 μf , the coil is energized at its resonant frequency which was experimentally found to be 3.5 mcps.

Initial experiments were concerned with reacting atomic hydrogen with solid nitric oxide at 77° K. It was found that impurities in the nitric oxide and in the hydrogen produced an apparent variety of compounds which condensed at 77° K to form varying shades of green, blue, and yellow solids. A literature survey revealed that the colors were likely due to a mixture of the compounds NO_2 , N_2O_3 , and N_2O_4 . These impurities were eliminated by the following procedure. The nitric oxide was slowly passed through two U-tube cold traps which were immersed in dewars containing a solid-liquid slush of 2-methyl pentane at -155° C. From the U-tube traps the nitric oxide entered a graduated test tube immersed in a dewar of liquid nitrogen where it condensed as a white solid. All impurities which condensed at -155° C were rejected. Any oxygen present would have reacted with the nitric oxide and condensed in the traps. The nitrogen was removed by the conventional freeze and thaw method.

Oxygen was removed from the hydrogen by passing the hydrogen over palladium asbestos heated to 400° C. The hydrogen then passed through a cold trap maintained at 77° K before entering the discharge tube.

A typical experimental run will now be described. After pumping the reaction system to 10^{-6} mm Hg, the purified nitric oxide was condensed on the inside bottom of the glass reactor at 77° K. Purified hydrogen at a pressure of 500-1000 μ Hg was allowed to impinge on the surface of the solid nitric oxide for a period of about forty minutes. This was done to determine if the hydrogen contained any impurities which would react with the nitric oxide and cause a visible color, phase, or pressure change. It has been found that when the oxygen is successfully removed from the

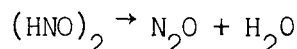
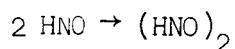
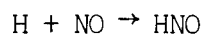
hydrogen, no apparent reaction occurs.

After the initial period of molecular hydrogen flow, the glow discharge is ignited to produce an atomic hydrogen flow. After a period of fifteen to twenty minutes the discharge is stopped and all uncondensed gases are pumped out of the reactor. The reaction products are examined for color and phase change at 77° K and also during the subsequent gentle warmup. It has been found that the reaction of hydrogen atoms with solid nitric oxide at 77° K produces a yellow solid which is formed on the surface of the nitric oxide. On removing the dewar of liquid nitrogen, the solid nitric oxide first evaporates and immediately afterward the yellow solid reaction product evaporates with such speed that it seems to explode. At the instant that the yellow solid "explodes," a click sound is produced inside the reactor. The yellow compound apparently decomposes because on recondensation of the gases only the white solid nitric oxide is formed.

The reaction of hydrogen atoms and nitric oxide has also been carried out at 90° K in liquid solution using propane as the solvent. The nitric oxide apparently does not react with the propane since the miscible solution of nitric oxide and propane can be subjected to fractional vacuum distillation which separates the components into the original unreacted species. The hydrogen atom reaction with the solution at 90° K produces a yellow precipitate similar in appearance to the yellow solid formed by the reaction of hydrogen atoms and solid nitric oxide at 77° K. On rapid warmup, the yellow precipitate seems to explode in much the same manner as the yellow solid.

The determination of the identity of the solution reaction products is complicated by the formation of the precipitate. A homogeneous liquid solution or slurry could be easily analyzed in the mass spectrometer since the liquid could be transferred from the glass reactor to the cold inlet system by use of a liquid nitrogen cooled pipet system described in previous reports. In further experiments with the liquid solution, a magnetic stirrer will be used in an attempt to maintain a homogeneous system during the course of the reaction. If this succeeds, the cooled pipet system can then be used.

A literature survey suggests that the yellow product has the formula HNO or $(\text{HNO})_n$. Harteck¹⁸ contacted hydrogen atoms and gaseous nitric oxide and condensed the products at liquid air temperature. A yellow deposit formed which explosively decomposed at higher temperatures to form N_2O and H_2O . From the amount of the decomposition products, Harteck suggested the empirical composition to be $(\text{HNO})_n$. The following sequence of reactions could have occurred:



HNO has often been suggested as an intermediate in reaction mechanisms.¹⁹

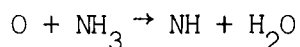
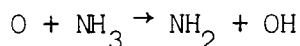
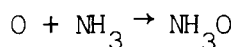
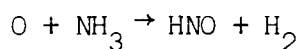
¹⁸P. Harteck, Ber. 66, 423 (1933).

¹⁹Laidler and Wojciechowski, Proc. Roy. Soc. A260, 103 (1961).

Dably²⁰ first identified HNO spectroscopically using flash photolysis of ammonia in the presence of nitric oxide. Brown and Pimentel²¹ decomposed methyl nitrite by photolysis to form formaldehyde and nitroxyl, HNO. They detected HNO by its infrared spectrum. The spectrum shows that the molecule contains a nitrogen-oxygen double bond, indicating that the structure is HNO and not HON.

D. Reactions of Atomic Oxygen

Another approach to synthesizing HNO, as well as NH_3O , is to react oxygen atoms with ammonia. It has been reported that ammonia will react with atomic oxygen at 90°C to form intensely yellow deposits which are uncharacterized but may contain the species HNO or NH_3O .^{22,23} It has also been reported that the species NH , NH_2 , NO and OH are present in a premixed atmospheric pressure flame of ammonia and oxygen.²⁴ The indicated species suggest the following reactions:



²⁰F. W. Dalby, "Symposium on Molecular Structure and Spectroscopy," Columbus Ohio, June 13, 1957.

²¹H. W. Brown and G. C. Pimentel, J. Chem. Phys. **29**, 883 (1958).

²²Geib, K. H., Naturwissenschaften, **15**, 44 (1936).

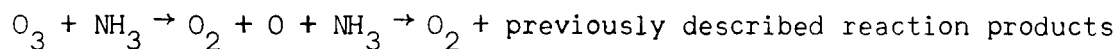
²³Harteck, P. and Kopsch, U., Z. Physik. Chem. **B12**, 327 (1931)

²⁴Forgarty, B. and Wolfhard, H., Nature **163**, 1122 (1951).

Since several of these species are present in the comae of comets, the reaction of oxygen atoms and ammonia is now being studied in order to better characterize the low temperature reaction products. The reaction system used in these experiments is the same system used in reacting hydrogen atoms and nitric oxide.

It has been found that oxygen atoms react with ammonia condensed at 90° K to form a light yellow layer of reaction products. At 77° K, this same reaction initially produces a light yellow layer, but as ozone is condensed from the discharged oxygen, the yellow layer becomes more intensely yellow and finally changes to an orange color. In another experiment, a layer of ozone was condensed on the bottom of the reactor at 77° K and a stream of gaseous ammonia was allowed to impinge on the ozone layer. A bright yellow deposit immediately formed. By pumping and slowly warming the reactor, the unreacted blue ozone was evaporated. As this was occurring, the bright yellow deposit again changed to an orange color. A thin layer of unreacted ammonia was condensed on the walls of the reactor and this layer also became yellow and then orange as the evaporating ozone passed over the condensed ammonia layer.

These experiments suggest two reaction possibilities. Either the ammonia is more reactive with ozone than with oxygen atoms or the ozone decomposes on contact with the ammonia forming a high concentration of oxygen atoms which then react with the ammonia according to the reaction



Again, by use of the low temperature inlet system of the mass spectrometer, the products formed during the course of the reaction can be identified.

III. PLANS FOR NEXT REPORTING PERIOD

Since the data developed in this laboratory (soon to be published) and that concurrently developed by others all seem to indicate that the free existence of low molecular weight compounds of divalent carbon are unlikely, we propose to use the same apparatus and technique that has been developed here to study the corresponding series of divalent silicon compounds. The synthesis of dimethyl silene, CH_3SiCH_3 , the silicon analog of a carbene has recently been reported as a short lived intermediate.²⁵ The data suggest that dimethylsilene is much less reactive than singlet CH_2 . Difluorosilene, SiF_2 , has also been recently observed as a transitory species. The generation, trapping and mass spectrometric identification and study techniques that have been developed here would be immediately applicable to those closely related systems. Silicon and carbon are of about equal magnitude (factor of 3 or so) in tables of cosmic abundancies.

The H and O atom reactions that were discussed above are to be repeated in a more controlled and more instrumented fashion by using the cryogenic inlet system.

In further experiments the identity of the yellow solid that was described above will be established by use of the mass spectrometer cold inlet system. O atoms also react with light hydrocarbons to produce usually red products which undergo frothy decompositions upon warming to still very low temperatures. These reactions will be carried out in the cold inlet system and the vapors produced during a slow controlled warmup

²⁵P. S. Skell and E. J. Goldstein, J. Am Chem. Soc. 86, 1442 (1964).

will be analyzed without warming beyond the temperature at which they appear, i.e., the temperature at which the solid or liquid exerts a vapor pressure of the order of 10^{-6} mm Hg.

Assuming that the unknown yellow solid has a stable vapor at some low temperature, further work using the mass spectrometer will permit us to assign a definite formula to the compound, possibly HNO, and to determine its bond energies from AP and IP measurements. Equivalent arguments can be made for the presently unknown red products from O atom reactions with light hydrocarbons.

In addition to reacting hydrogen atoms with nitric oxide, we also will be reacting hydrogen atoms with cyanogen, methane, ammonia, carbon monoxide, and other simple compounds of carbon, nitrogen, and oxygen. The best experimental procedure for this work now appears to be to first carry out the reaction in the system now in use, observing the gross reaction changes. The more successful and interesting reactions will then be more carefully studied using the low temperature inlet system of the mass spectrometer.